Effect of Protonated Organic Cations and Anion-pi Interactions on the Magnetic Behavior of Hexabromorhenate(IV) Salts

The effect of protonated organic cations and anion-π interactions on the magnetic behavior of hexabromorhenate(IV) salts

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Supporting Information Placeholder

ABSTRACT: Two novel Re^{IV} compounds of formulae $(Hbpym)_2[Re^{IV}Br_6]\cdot 4H_2O$ (**1**) and $(H_4biim)[Re^{IV}Br_6]\cdot 4H_2O$ (**2**) [$Hbpym^+$ = 2,2'-bipyrimidinium cation and H_4biim^{2+} = 2,2'-biimidazolium dication] have been prepared and magneto-structurally characterised. **1** and **2** exhibit distinct crystal packing, and the presence of weak intermolecular contacts, such as Re-Br···Br-Re (**1** and **2**), Re-Br···(H_2O)···Br-Re (**1** and **2**) and Re-Br···π···Br-Re (**2**), lead to different magnetic behaviors. While **1** is antiferromagnetic, **2** is a ferromagnetic compound and indeed the first example of ferromagnetic salt based on the hexabromorhenate(IV) anion. These results suggest a straightforward synthetic route to the preparation of new ferromagnetically coupled Re^{IV} compounds.

Non-covalent interactions involving aromatic rings, such as π···π and cation···π contacts, are extremely important in the field of supramolecular chemistry, playing key roles in well-known chemical and biological processes.[1] In recent years, the anion···π interaction, which is a weak force generated between anions and electron-deficient aromatic systems, has also been recognized as a non-covalent bonding interaction.[1e,f] The nature of this *new* supramolecular bond has been described by numerous theoretical studies and several experimental investigations focused on, for instance, anion recognition and materials science.[1]

The multidisciplinary field of molecule-based magnetism has mostly focused on the investigation of magnetic materials in which the interactions are transmitted *via* chemical bonds through superexchange interactions.[2,3] However, magnetic interactions can also be mediated through space *via* non-covalent forces, as observed in systems such as organic radicals and charge-transfer salts, where the spin carriers are not chemically connected by means of bridging ligands. In some cases these systems can even display 3D magnetic ordering.[2,3] In this respect, the development of salts containing complexes of highly anisotropic 4d and 5d metal ions has been surprisingly scarce,[4] despite these metal ions exhibiting more diffuse magnetic orbitals than those of their 3d analogues, which could a priori enhance the through-space interactions.[4,5]

The magnetic properties of the mononuclear hexahalorhenate(IV) anions, of general formula $[ReX_6]^{2-}$ (X = F, Cl, Br, I), have been thoroughly investigated for decades.[6] In general, hexahalorhenate(IV) salts of diamagnetic, univalent cations show significant antiferromagnetic interactions, which are transmitted in the crystal lattice of these systems through Re–X···X–Re intermolecular contacts, between the paramagnetic and highly anisotropic Re^{IV} centres ($5d^3$ ion with t_{2g}^3 configuration).[6] Given that the intermolecular halogen···halogen distance depends on the countercation size, bulky organic cations such as tetraphenylarsonium $(AsPh_4)^+$ and tetra-*n*-butylammonium $(NBu_4)^+$ preclude the magnetic coupling between adjacent hexahalorhenate(IV) anions.[6] However, paramagnetic cations can also provide new insights into the magnetic properties of this family of materials, indeed studies of hexachlororhenate(IV) salts of organic radicals,[7a] organometallic ferrocenium[7b] and ruthenium(III)[7c] cations revealed the occurrence of other magnetic phenomena, such as ferromagnetism and spin canting.[6,7c] The most investigated $[ReX_6]^{2-}$ salts to date are those obtained with the hexachlororhenate(IV) anion. In comparison, the magnetic properties of compounds based on the heavier hexabromo- and hexaiodorhenate(IV) salts have been much less studied.[7b,8]

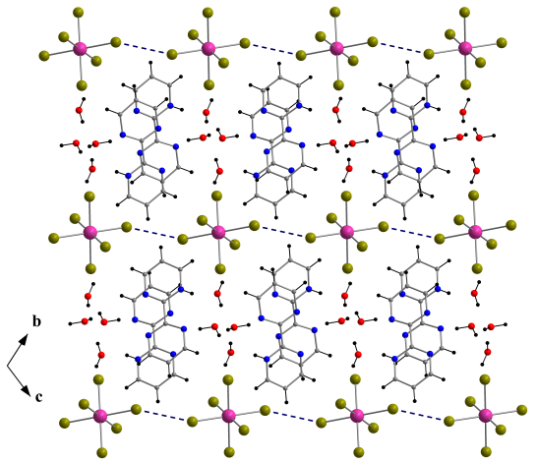

Figure 1. View of the arrangement of protonated $(Hbpym)^+$ cations and $[ReBr_6]^{2-}$ anions of **1**, highlighting the Br···Br

intermolecular interactions (dashed lines). Color code: pink, Re; olive green, Br; blue, N; red; O; grey, C; black, H.

Herein we report the synthesis and magnetostructural study of two novel Re^{IV} compounds of formulae $(Hbpym)_2[Re^{IV}Br_6]\cdot 4H_2O$ (**1**) and $(H_4biim)[Re^{IV}Br_6]\cdot 4H_2O$ (**2**) [$Hbpym^+$ = 2,2'-bipyrimidinium cation and H_4biim^{2+} = 2,2'-biimidazolium dication]. The two salts exhibit distinct crystal packing and display markedly different magnetic properties. Remarkably, **2** is the first example of compound based on the $[ReBr_6]^{2-}$ anion displaying ferromagnetic behaviour. Compounds **1** and **2** are synthesised from $K_2[ReBr_6]$ in a 0.5 M HBr solution and in the presence of protonated 2,2'-bipyrimidine ($Hbpym^+$) and 2,2'-biimidazole (H_4biim^{2+}) cations, respectively. While crystals of **1** are obtained in 2-3 weeks after slow evaporation at room temperature, those of **2** grow in a few days by standing in the fridge at 3°C (see the Supporting Information for full details).

1 and **2** crystallise in the triclinic system with space group *P*$\bar{1}$, (Table S1). Their structures are made up of the hexabromorhenate(IV) anion $[ReBr_6]^{2-}$ (**1** and **2**), organic $(Hbpym)^+$ (**1**) and $(H_4biim)^{2+}$ (**2**) cations and water molecules (**1** and **2**) which are self-assembled through an extended network of hydrogen bonds, Br···Br and Br···π type intermolecular interactions (Figs. 1 and 2). Each Re^{IV} ion in **1** and **2** is six-coordinate, bonded to six bromide ions in a *quasi* regular octahedral geometry. No significant differences are seen in the Re–Br bond lengths [the average value being 2.515(1) (**1**) and 2.509(1) Å (**2**)], in agreement with those found in previously reported compounds containing the anionic $[ReBr_6]^{2-}$ unit.[8] The $(Hbpym)^+$ and $(H_4biim)^{2+}$ cations are *quasi* planar and strictly planar, respectively, and in the case of the $(H_4biim)^{2+}$ cation an inversion centre is present at the middle of the inter-ring C–C bond. The average C–C and C–N bond length values agree with those found in previously reported salts.[9]

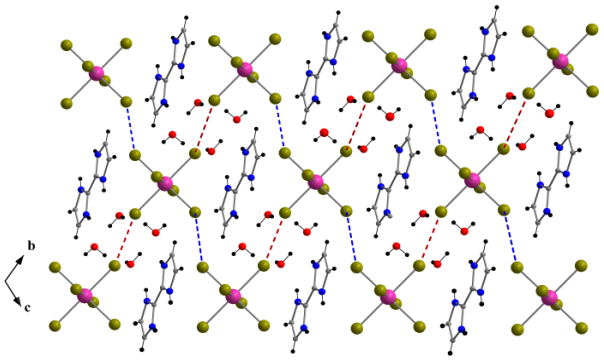

Figure 2. View of a fragment of the crystal packing of **2** highlighting the supramolecular 2D (dashed red lines) and 3D (dashed red and blue lines) networks generated through Br···Br interactions. Color code: pink, Re; olive green, Br; red, O; blue, N; grey, C; black, H.

In the crystal packing of **1**, the shortest Br···Br contacts of 3.748(1) and 3.813(1) Å direct two alternate chains of $[ReBr_6]^{2-}$ anions which grow along the crystallographic a axis (Figure S1). Additional longer Br···Br interactions of 4.006(1) Å between these chains generate sheets of $[ReBr_6]^{2-}$ anions (Figure S1), which are separated from each other by a layered structure of $(Hbpym)^+$ cations and water molecules (Figure 1). π···π type interactions between the aromatic rings of neighbouring $(Hbpym)^+$ cations [the shortest intercentroid distance being *ca*. 3.9 Å] contribute to stabilizing the crystal structure in **1** (Fig. S2). In **2** the shortest Br···Br contact of 3.583(1) Å results in anionic chains that grow along the crystallographic *b* axis. Additional Br···Br interactions of 3.619(1) and 3.726(1) Å between $[ReBr_6]^{2-}$ anions generate 2D and 3D structures, respectively (Figures 2 and S3). No π···π type interactions between the rings of $(H_4biim)^{2+}$ molecules are observed in **2**. Instead, Br···π contacts [average Br···π distance of approximately 3.42 Å] occur, leading to a one-dimensional motif of alternating cations and anions (Figure 3). In addition, a branched-chain motif of water molecules and a tetrameric $(H_2O)_4$ ring are also present in the crystal structures of **1** and **2**, respectively (see Figure S4, Table S2, and Table S3).

Dc magnetic susceptibility measurements were carried out on microcrystalline samples of **1** and **2** in the 2-300 K temperature range, under external magnetic fields of 0.1 T (at $T > 30$ K) and 0.025 T (at $T < 30$ K). The $\chi_M T$ *vs*. *T* plots of **1** and **2** are given in Figures S5 and 4, respectively. At room temperature the $\chi_M T$ values are 1.58 (**1**) and 1.59 $cm^3\ mol^{-1}\ K$ (**2**), which are as expected for a magnetically isolated Re^{IV} ($5d^3$, $S = 3/2$ with t_{2g}^3 configuration) mononuclear complex with $g = 1.8–1.9$.[6-8,10] Upon cooling, $\chi_M T$ for **1** remains practically constant until 50 K, then decreases at lower temperatures reaching a minimum value of 0.88 $cm^3\ mol^{-1}\ K$ at 2.0 K. No maximum of the susceptibility is observed in **1** (inset in Fig. S5). In contrast, $\chi_M T$ for **2** decreases slowly at first and then more abruptly with decreasing temperature reaching a minimum value of 1.02 $cm^3\ mol^{-1}\ K$ at 7.5 K. It then increases to a maximum value of *ca*. 1.54 $cm^3\ mol^{-1}\ K$ at 2.0 K. Given that the minimum value of $\chi_M T$ is somewhat higher than 1.0 $cm^3\ mol^{-1}\ K$ (typical value found in magnetically isolated Re^{IV} mononuclear complexes),[6] the occurrence of a ferrimagnetic behaviour in **2** is ruled out. The decrease in the $\chi_M T$ values observed for **1** and **2** is likely due to the presence of intermolecular interactions and zero-field splitting (zfs) effects,[6-8,10] whereas the observed increase for **2** at low temperature indicates the occurrence of an unprecedented intermolecular ferromagnetic coupling in a hexabromorhenate(IV) salt.

The field dependence of the molar magnetisation (*M*) plots for **1** and **2** at 2.0 K are given in Figure S6, which exhibit continuous increase of *M* with applied magnetic field, the increase being faster for **2**. No hysteresis loop is observed. The comparison of the magnetisation plots also supports the presence of a weak ferromagnetic exchange in **2**, because the maximum value of *M* obtained per rhenium(IV) ion (*ca*. 1.8 μ_B) is somewhat above that of magnetically isolated Re^{IV} complexes (*ca*. 1.6 μ_B).[6]

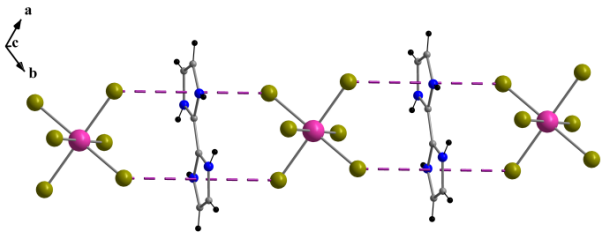

Figure 3. Detail of the one-dimensional motif generated by intermolecular Re-Br···π···Br-Re interactions of alternate cations and $[ReBr_6]^{2-}$ anions in **2**.

In order to analyse the magnetic behaviour of **1** and **2**, we have used the Hamiltonian of eq(1) (Fig. S7) and its derived theoretical expression for the magnetic susceptibility,[2b] including a θ term to account for the observed intermolecular interactions (Fig. S7). Best least-squares fits of the experimental data in the 2-300 K temperature range afforded the parameters: $|D|$ = 5.8 cm^{-1}, g = 1.85 and θ = - 0.60 K (- 0.42 cm^{-1}) with R = 1.3 x 10^{-5} for **1**, and $|D|$ = 6.1 cm^{-1}, g = 1.88 and θ = + 1.05 K (+ 0.73 cm^{-1}) with R = 4.5 x 10^{-5} for **2** {R being the agreement factor defined as $\Sigma_i[(\chi_M T)_i^{obs} - (\chi_M T)_i^{calc}]^2 / [(\chi_M T)_i^{obs}]^2$}. The theoretical curves (red solid lines in Figs. S5 and 4) match the experimental data well in the studied temperature range; the g and D values obtained for **1** and **2** are in agreement with those previously reported for compounds based on the $[ReBr_6]^{2-}$ anion.[8]

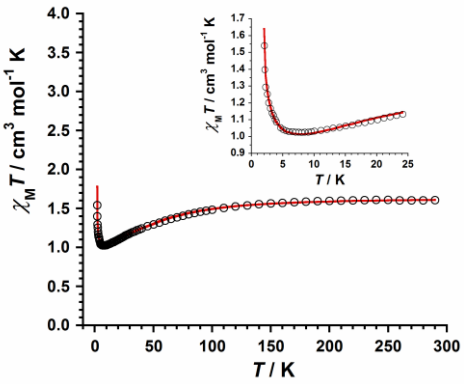

Figure 4. Plot of the $\chi_M T$ product *vs*. T for **2**. The solid red line represents the best-fit of the experimental data. The inset shows the low temperature range (2-25 K).

Negative (**1**) and positive (**2**) θ values were obtained from the fit, which indicate the occurrence of dominant antiferro- and ferromagnetic exchange for **1** and **2**, respectively. In comparison, the magnetic dipolar contribution, assuming parallel moments (E_{dip} being – 0.019 and – 0.012 cm^{-1} for **1** and **2**, respectively),[11] can be considered much less significant for both compounds. Given that the paramagnetic $[ReBr_6]^{2-}$ entity is the same in **1** and **2**, the different magnetic behavior observed in both compounds can be assigned to the distinct spatial arrangement of the organic cations in the crystal. The crystal packing of both compounds displays a number of important intermolecular interactions, including Re-Br···Br-Re (**1** and **2**), Re-Br···(H_2O)···Br-Re (**1** and **2**), and Re-Br···π···Br-Re (**2**) contacts, between the paramagnetic $[ReBr_6]^{2-}$ units (Table S4). It is well-known that short Re-Br···Br-Re intermolecular interactions can transmit antiferromagnetic exchange between the metal centres,[6-8,10] which likely explains the negative θ value found for **1**. However, Re-X···(H_2O)···X-Re and Re-X···π···X-Re (X = halogen atom) type contacts are uncommon in Re^{IV} systems. Indeed, the Re-X···π···X-Re interaction has only been seen once before, in the previously reported $(H_4biim)[ReCl_6]\cdot 4H_2O$ (**3**) compound, which is a ferromagnetic salt isostructural to **2**.[10] Hence, it seems the Re-X···π···X-Re interaction is at the origin of the unusual ferromagnetic exchange, which would be mediated *via* a ~~through-space~~ spin polarization mechanism through the protonated imidazole rings of the $(H_4biim)^{2+}$ cation (Fig. 5). In fact, each Re^{IV} ion possesses three unpaired electrons (S_{Re} = 3/2) occupying the t_{2g} (d_{xy}, d_{yz}, d_{zx}) magnetic orbitals of π-type symmetry. These π electrons are largely delocalized onto the Br donor atoms. Because of the occurrence of close Br···π contacts among the $[ReBr_6]^{2-}$ anions and $(H_4biim)^{2+}$ cations, they partially polarize the π electron cloud of the two imidazolium rings leading to an alternance of the spin densities at the adjacent nitrogen and carbon atoms. In that case, the spin densities at the Br atoms possess the same sign as those at the metal atoms due to the spin delocalization in the Re–Br bonds, while the imidazolium-nitrogen and carbon atoms show opposite negative and positive spin densities, respectively (Fig. 5). Hence, the concerted double spin polarization (DSP) by the unpaired π electrons of the Re^{IV} ions from the $[ReBr_6]^{2-}$ anions across the $(H_4biim)^{2+}$ cations are additive for a parallel spin alignment, favoring then a ferromagnetic coupling, as observed experimentally. Finally, if we compare the positive θ value of **2** (θ = + 1.05 K) and **3** (θ = + 0.58 K), we observe that the θ value of **2** is almost twice that of **3**.[10] Given that the X···π distances are quite similar in both compounds [the average X···π distance being approximately 3.4 (**2**) and 3.3 (**3**) Å], the different nature of the halogen atom [Br (**2**) *vs*. Cl (**3**)] would account for the larger θ value found in **2** with respect to that in **3**.

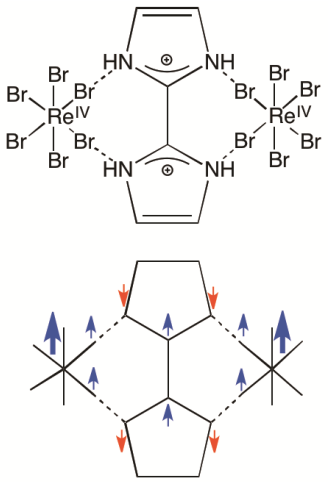

Figure 5. (Top) Schematic of the intermolecular Re^{IV}-Br···π···Br-Re^{IV} interaction, which generates chains of cations and anions in **2**. (Bottom) Schematic drawing of the spin polarization through the protonated imidazole rings between adjacent $(H_4biim)^{2+}$ cations and $[ReBr_6]^{2-}$ anions in **2**. The two big arrows are the unpaired electrons of the metal atoms, while the small arrows represent the spin-polarized π-electron system of the $(H_4biim)^{2+}$ cation, the up and down arrows indicating positive and negative spin densities, respectively.

In summary, two novel mononuclear Re^{IV} compounds of formula $(Hbpym)_2[ReBr_6]\cdot 4H_2O$ (**1**) and $(H_4biim)[ReBr_6]\cdot 4H_2O$ (**2**) have been prepared and magneto-structurally studied. A distinct spatial arrangement of the protonated organic cations occurs in the crystal lattice of both compounds. While sheets of cations and anions are found in **1**, the cations and anions intercalate generating packed chains in **2**. The presence of weak intermolecular contacts, such as Re-Br···Br-Re (**1** and **2**), Re-Br···(H_2O)···Br-Re (**1** and **2**) and Re-Br···π···Br-Re (**2**) lead to different magnetic behaviors. While **1** is antiferromagnetic, **2** is a ferromagnetic compound. Indeed, **2** is the first example of ferromagnetic salt based on the $[Re^{IV}Br_6]^{2-}$ anion. In addition, we have found in the literature that most of the reported paramagnetic metal systems exhibiting anion···π interactions are based on salts where the anions (for instance, BF_4^-, Cl^-, ClO_4^-, NO_3^-, PO_4^{3-}, etc) are diamagnetic and the π contribution comes from heterocyclic ligands coordinated to the transition metal,[1] which strongly affects the π-acidity of the aromatic ligand, thus increasing the strength of the anion···π interaction. Given that the $[ReBr_6]^{2-}$ anion is paramagnetic and the π contribution in **2** comes from the diamagnetic $(H_4biim)^{2+}$ cations, we have reported here a new example of system that exhibits this type of interaction.

Finally, these results suggest a straightforward synthetic route to the preparation of new ferromagnetically coupled Re^{IV} compounds, a strategy which could also be extended to other anisotropic 4d and 5d metal ions.

Supporting Information

Preparation of **1** and **2**, Tables S1-S4, and Figures S1-S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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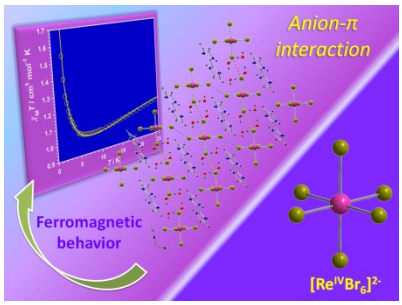
SYNOPSIS TOC



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